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VISCOSITY AND OTHER PROPERTIES OF DEXTRIN-BORAX-ALKALI SOLS.

By

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Summary.

When aqueous suspensions of highly soluble pyrodextrins containing borax are treated with sodium or potassium hydroxide the viscosity rises steeply until about 2·7 mols hydroxide per mol borax have been added, and then decreases rapidly with increased amounts of caustic alkali. Viscosity-temperature and viscosity-concentration curves indicate increasing association on the rising portion of the curve of viscosity against mols alkali added, but the pH, specific rotation, refractive index, and density, show no marked fluctuations in the neighbourhood of the peak of the viscosity curve. Comparison of the physical properties of glucose-borate and dextrin-borate sols indicates that the mechanism of complex formation in dextrin-borate pastes is different from that operating in the well-known glucose-borate complexes.

Introduction.

The increase in viscosity effected by adding borax ($Na_2B_4O_7.10H_2O$) to aqueous dispersions of starch and its modifications (*e.g* dextrins) has long been known. It is also common knowledge in the adhesives industry that the addition of sodium hydroxide greatly increases the thickening effect of borax. Though such dextrin-borax-alkali glues are manufactured in large quantities published data on the relation between alkali-content and viscosity are very scanty, and authorities differ widely in the amount of sodium hydroxide recommended. Thus Dulac (5) uses 3·9% sodium hydroxide on the weight of borax, while Radley (13) states that " The borax . . . . . is generally added to the extent of twice the weight of alkali " (sodium hydroxide). Hoeppler (9) recommends a glue containing 100 parts dextrin, 10 parts borax, and one part sodium hydroxide. Frieden (7) says, " When used with an adhesive containing borax, the effect of caustic soda is to increase the viscosity and the rate of development of tack still further. This effect is particularly notice-

able for small amounts, *e.g* 0·2 to 0·5%. Amounts larger than 1% are inadvisable." The basis for calculating the percentage of alkali is not stated.

The present work was undertaken to clarify the relations between the amount of sodium hydroxide added and the pH and viscosity of dextrin-borax-alkali glues, and to relate the results as far as possible to the findings of the many previous workers who have studied the complexes formed by boric acid and its salts with polyhydroxy compounds.

Materials.

Two dextrins were mainly used—a yellow potato dextrin, manufactured by N. V. Meyer (Holland), and a yellow maize dextrin (Dextrines, Ltd. ; Ref. 2). Both were almost completely (95–100%) soluble in cold water, and are typical of the dextrins used commercially in making dextrin-borax-alkali glues. Some experiments were also performed with another yellow potato dextrin (Elliott & Crabtree, Ltd., Ref. No. 1180), and with a wheat dextrin of somewhat lower solubility (70–80%) made in this factory. Since the results with these latter samples were similar to those obtained with the others, they will not be further discussed.

The borax and sodium hydroxide were both of chemically pure grade, yielding on analysis 101·5% $Na_2B_4O_7.10H_2O$ (probably a result of slight efflorescence), and 98·5% NaOH, respectively. The glycerol was of B.P. and the glucose of U.S.P. quality.

Methods.

In industrial practice glues of this type are made by heating the appropriate quantities of dextrin, borax, and water, to 80°–90°, and then shutting off steam before addition of sodium hydroxide. In the laboratory the borax, dextrin, and water, were heated for 10 mins. with constant stirring in a boiling-water bath. Then either (*a*) the sodium hydroxide solution was added and the mixture kept for 5 mins. longer at 100°, or (*b*) the glue was allowed to cool to room temperature before adding the alkali. The slight difference between the viscosities of corresponding glues prepared according to these two methods will be discussed below. pH measurements were made at 20° with a glass electrode and a Beckmann Model M meter, and were corrected for the sodium ion effect. Densities, refractive indices, and optical activities, were determined by standard methods. Glue viscosities were measured with the Brabender Recording Viscosimeter (16), an instrument which has been found very satisfactory with glues of high viscosity (up to 250 poise) and anomalous (plastic) flow. As the graph of scale reading against speed of rotation showed, the glues examined in this research were all true liquids, except for some slight thixotropic breakdown with the maize dextrin glues, and consequently the viscosity could be directly calculated from the scale reading, using conversion factors derived with standard oils. Since the instrument has no means of temperature control, glue samples were brought to 20° before measuring viscosities. This procedure is adequate for the somewhat limited precision of the instrument (16), and more than adequate for measuring viscosity differences of the order dealt with in this paper. Viscosity measurements for the curves of log ν against 1/T, and

for the glucose, glycerol, and maltose solutions, were made with Ostwald viscometers (BSS. No. 188 (1937)).

In the results " dextrin " refers to the anhydrous substance, " borax " and " sodium hydroxide " to the materials described above.

Dextrin concentrations are given in grams of dextrin per 100 grams of glue.

RESULTS.

pH Relationships.. All commercial pyrodextrins have a decided acid reaction. The titration curves of the maize and potato dextrins used in this work (Fig. 1) show that the acidity cannot be attributed to any one component. It is probably

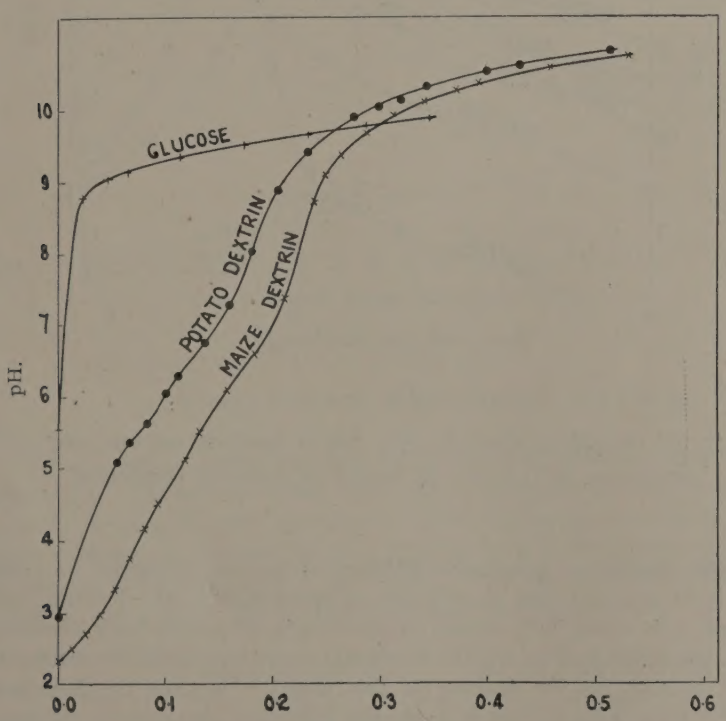

Fig 1.

Potentiometric titration curves of dextrins and glucose.

due to the combined effect of (*a*) residual traces of the acid used in dextrinization (*b*) acidic phosphates, naturally present in maize and potato starches, (*c*) fatty acids (in maize starch), (*d*) carboxyl groups formed by oxidation during dextrinization (10), and (*e*) the weakly acidic properties of the glucosidic hydroxyls (8, 12).

This last effect may be responsible for the appreciable depression of the pH in the upper part of the curve. A similar titration curve for glucose is included for comparison.

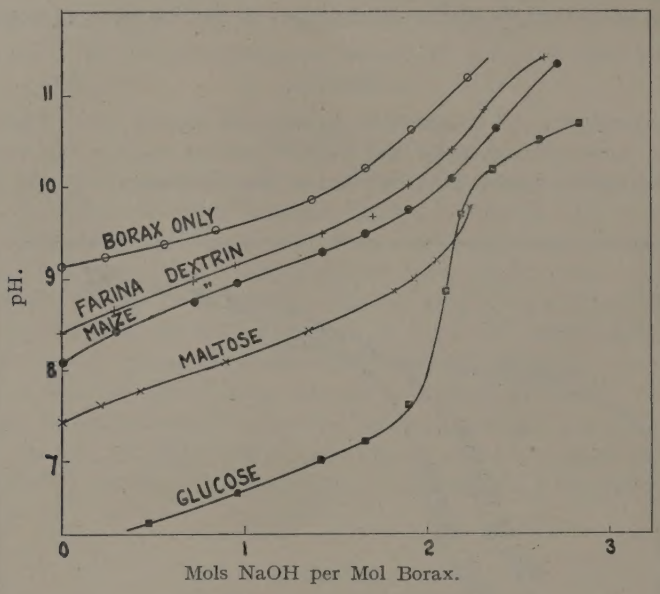

Fig. 2.

Changes in pH on adding alkali to 25% sols of dextrins, maltose, and glucose, containing 10% borax on weight of hydroxy compound.

The pH changes on progressive addition of sodium hydroxide to a solution of borax (3·81 gm./lit.), and to 25% sols of maize and potato dextrins, maltose, and glucose, containing 10% borax on the weight of polyhydroxy compound in each case, are shown in Fig. 2. The significant point here is the decreasing ability of glucose, maltose and the dextrins (in that order) to increase the dissociation of boric acid. Only with glucose is a marked inflection obtained on reaching the $NaBO_2$ stage.

Viscosities. Sodium hydroxide added to cold dextrin pastes in concentrations much greater than is customary in dextrin-borax-alkali glues, has no marked effect on the consistency. Even on heating there is only a slight fall in viscosity, probably due to oxidative degradation. In the presence of borax however, the results are very different. Fig. 3 shows the results obtained with a potato dextrin. They are entirely representative of those obtained with all the dextrins examined.

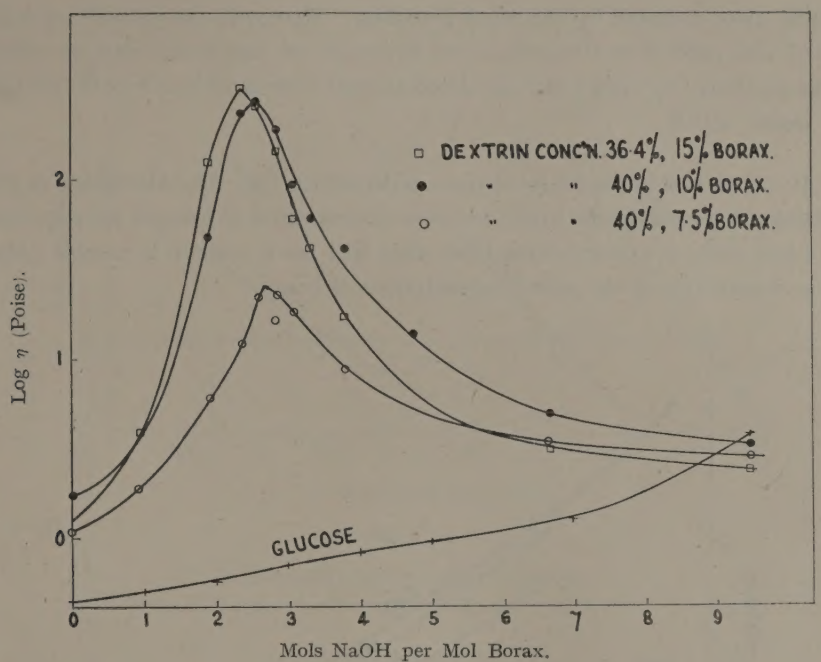

Fig 3.

Viscosity curves of potato dextrins and glucose.

The sharp maximum at 2·4–2·85 mols sodium hydroxide per mol borax was unexpected. From the many experiments performed it was evident that the position of the peak does not depend on the dextrin concentration, but there is a slight tendency for the maximum to occur at lower sodium hydroxide : borax ratios as the percentage of borax is increased. That the maximum viscosity does not occur at any definite pH is shown by the following results

% borax on dextrin.	pH at peak viscosity.
5·7	10·25
11·4	10·42
17·1	10·8 (maize)
	11·0 (potato)

The use of potassium hydroxide instead of sodium hydroxide gives a peak in the viscosity curve at the same molar ratio of hydroxide to borax.

Alkaline degradation of the dextrin in the hot medium as a major cause of the steep fall in viscosity after passing the peak was excluded by cooling the dextrin-borax paste to 20°–25° before adding the sodium hydroxide (method (*b*)). Viscosities of glues prepared by this method were only slightly higher than those of the corres-

ponding glues prepared by the usual procedure. Moreover, the viscosity of a glue treated with more than 2·8 mols sodium hydroxide per mol borax could be restored to the maximum by adding the calculated amount of hydrochloric acid to neutralise the excess alkali.

It was noticed in the course of these experiments that the viscosities of glues containing 2–3 mols sodium hydroxide were more sensitive to changes of temperature and particularly of concentration than those with lower sodium hydroxide : borax ratios, irrespective of the actual concentration of borax.

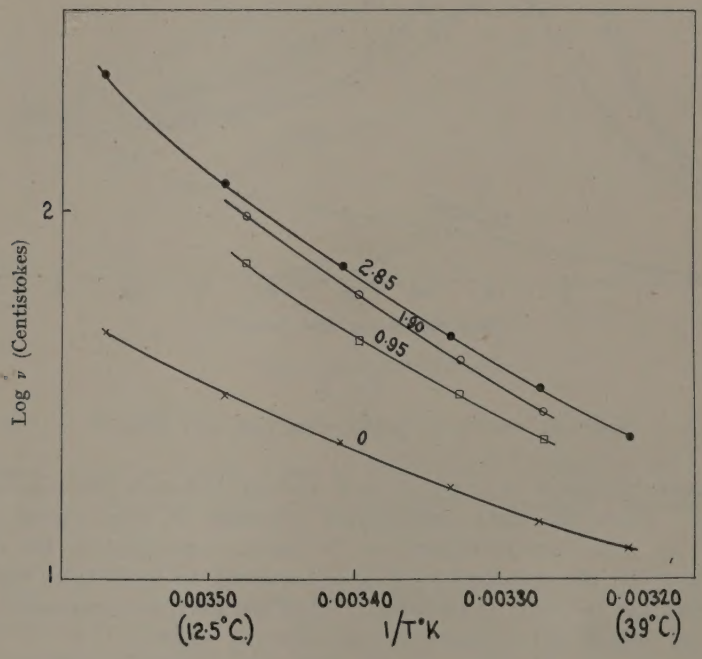

Fig 4.
Viscosity-temperature curves.

Fig. 4 shows the plot of log ν (cs)* against 1/T°K. for a potato dextrin sol containing 26·1% dextrin with 10% borax on the weight of dextrin and varying molecular proportions of sodium hydroxide. There is an increase in the slope of the curve on adding 0·95 mols hydroxide, but practically no further change on adding up to 2·85 mols hydroxide per mol borax. All curves show appreciable deviations from linearity. The significance of this will be discussed below.

* η (poises) = ν (stokes) × density.

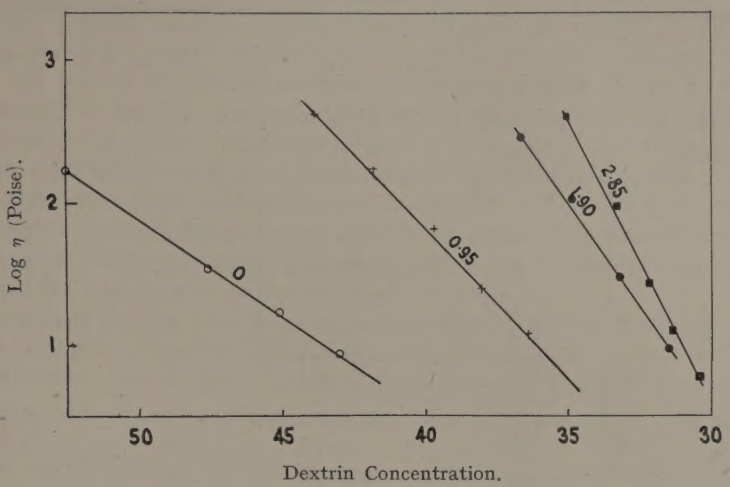

Fig. 5.
Viscosity-concentration curves.

Fig. 5 illustrates the dependence of log η on concentration for potato dextrin glues containing 11·4% borax on the weight of dextrin, for higher viscosities in the commercially useful range. There is a steady increase in the slope of the curves as the proportion of hydroxide increases. Other experiments (not shown) indicated that the slopes of the log η against C curves for glues containing 6, 8, and 11%, borax on the weight of dextrin, and 2·38 mols sodium hydroxide per mol borax, were equal and intermediate between the slopes of the curves with 1·9 and 2·85 mols hydroxide in Fig. 5.

Other Physical Properties. It seemed possible that the density, optical rotation, or refractive index, of these glues might have abnormal values in the neighbourhood of the peak in the viscosity curve. Borax and borates are known to have a very marked effect on the optical activity of glucose solutions (4, 15), though their effect on the specific rotation of maltose is slight (3). The table gives the results of these experiments.

TABLE I.

% borax on dextrin	Mols NaOH per mol borax	$[\alpha]_D$ (8·75% sol at 17°)	n_D (21·8% sol at 17°)	Δ (29·1% sol at 21·5°)
0	0	179·5	1·3812	1·1265
11·45	0	179·0	14	1·1455
,,	0·95	179·3	24	1·1495
,,	1·9	179·0	34	1·1541
,,	2·85	174·0	39	1·1589
,,	3·8	175·8	—	1·1629
,,	4·75	175·0	53	1·1665
,,	6·65	170·3	70	1·1733
,,	9·5	168·5	91	1·1869

Density and refractive index are linear functions of the sodium hydroxide concentration over the entire range. The specific rotation shows no change till more than two mols sodium hydroxide have been added. The slight decrease thereafter may be due to isomerization (6), since the alkaline sols were allowed to stand overnight before polarization.

DISCUSSION.

The thickening action of borax on starch and dextrin dispersions is assumed by Frieden (7) to be due to " association of the borax and dihydrotetraboric acid molecule with some of the remaining water, to the coupling of the borax molecules with the dextrin molecules, or to both." A similar viewpoint is adopted by Schoch (14), who points out that the ionization of boric acid is increased by the addition of starch or dextrin, and conjectures that the increase in viscosity " may well be related to the complex formation between borate ion and such polyhydroxylated substances as glycerol, glucose, and mannitol."

The increase in the viscosity of dextrin-borax pastes on adding up to 2·5 mols sodium hydroxide per mol borax is so great relative to the amount of borate present that it can safely be said that association of the borate with some of the remaining free water is of minor importance compared with the association of the dextrin molecules. Mere withdrawal of water would not account for the marked changes in the viscosity-temperature and viscosity-concentration curves (Figs. 4 and 5) with increasing amounts of sodium hydroxide. The appreciable curvature of the lines obtained when log v is plotted against $1/T$ is further evidence of association.

If increased viscosity be taken as a measure of complex formation between dextrin and borate it is evident from Fig. 3 that the molecule or ion responsible for promoting association is the metaborate, and that borates of lower alkali-content

are effective only in proportion to the amount of $NaBO_2$ they may be regarded as containing. This has also been established for the sugars (4, 11), and the formation of a loose association compound, readily dissociated on heating or dilution, between dextrin and sodium metaborate accounts well for the results illustrated in Figs. 3, 4, and 5. The fact that the peak viscosity with dextrins occurs at rather more than the two mols sodium hydroxide needed to form the metaborate is probably due to part of the hydroxide going to neutralise the acidic dextrin. The weight of sodium hydroxide needed to bring the dextrin alone to pH 10·5 (Fig. 1), added to that needed to convert the borax to metaborate, shows that the peak viscosity should occur at about 2·4 mols hydroxide per mol borax, in reasonably good agreement with the experimental figure of 2·4–2·85 mols.

To account for the large increase in viscosity of dextrin pastes on adding metaborate at least two dextrin molecules must be associated through each metaborate molecule. The extensive work of Boeseken and his school (1) has shown that many diols form complexes of the type $\left[\begin{matrix}=CO\\ |\\ =CO\end{matrix}\!\!>\!B\!<\!\!\begin{matrix}OC=\\ |\\ OC=\end{matrix}\right]^-H^+$ with the hydrated form $\left[\begin{matrix}HO\\ HO\end{matrix}\!\!>\!B\!<\!\!\begin{matrix}OH\\ OH\end{matrix}\right]^-H^+$ of boric acid. Progressive neutralisation of boric acid will lead to a rapid increase in the concentration of the $\left[\begin{matrix}HO\\ HO\end{matrix}\!\!>\!B\!<\!\!\begin{matrix}OH\\ OH\end{matrix}\right]^-$ ion and of the diol complex, resulting in an increase in viscosity up to the metaborate stage, when the composition of the system may be represented as $\left[\begin{matrix}=CO\\ |\\ =CO\end{matrix}\!\!>\!B\!<\!\!\begin{matrix}CO=\\ |\\ CO=\end{matrix}\right]^-Na^+$ Larger amounts of sodium hydroxide will then, by tending to form Na_2HBO_3 and Na_3BO_3 cause dissociation of the complex, with the fall in viscosity actually observed.

Some indication of the point of attachment of the metaborate ion to the glucose ring is afforded by the observation of Levy and Doisy (11) that the reducing group of glucose is necessary for complex formation with borates. In equal weights of 1 : 4 α-polyglucosides of different degrees of polymerization the average number of reducing groups per glucose unit will decrease with increasing size of the molecule, whereas the number of free No. 2 or No. 3 carbon atoms per glucose residue will be independent of molecular weight. The results of Fig. 1, showing that the ability of polyglucosides to increase the dissociation of boric acid diminishes from glucose to dextrin, and those given in the table, which show that borax has no effect on the optical rotation of dextrin, compared with a slight effect on maltose (3) and a marked effect on glucose (15), thus suggest that the reducing group of the dextrin molecule is involved in complex formation with borates.

This general analogy between the dextrins and the simpler sugars does not, however, extend to their viscosity behaviour. Fig. 3 shows the viscosity curve (in centistokes x 10^2) for a 50% glucose solution containing 10% borax on the weight of sugar. Maltose in 50% concentration and glycerol in 60% concentration gave similar curves, the steady rise in viscosity in all cases being easily accounted for by the progressive replacement of water by sodium hydroxide.

No satisfactory explanation of the difference between the two types of curve can be put forward at present. It is, however, very probable (2) that dextrin contains

much more complicated molecules than simple chains of 1 : 4 α-glucose units, and it may be supposed that the metaborate ion can associate with such molecules at more than two points, thus enabling a chain of alternate dextrin and metaborate molecules to be formed. The viscosity of the sol would be greatly increased by the presence of long chains of this type, but would at the same time be very sensitive to dissociation of a relatively small proportion of the metaborate linkages by heat, dilution, or excess of sodium hydroxide. It is hoped to carry out further work on this point.

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